

PRODUCTION OF HYDROCYANATION CATALYSTS

CROSS-REFERENCE TO PRIORITY/PCT APPLICATIONS

[0001] This application claims priority under 35 U.S.C. § 119 of FR-98/16469, filed December 22, 1998, and is a continuation of PCT/FR99/03232, filed December 21, 1999 and designating the United States (published in the French language on June 29, 2000 as WO 00/37174; the title and abstract were also published in English), both hereby expressly incorporated by reference.

CROSS-REFERENCE TO COMPANION APPLICATION

[0002] Our copending application Serial No. _____ [Attorney Docket No. 022701-933], filed concurrently herewith, assigned to the assignee hereof and also expressly incorporated by reference.

BACKGROUND OF THE INVENTION

Technical Field of the Invention:

[0003] The present invention relates to a process for the production/manufacture of a catalyst useful for the hydrocyanation of ethylenically unsaturated organic compounds.

[0004] This invention more especially relates to a process for the production/manufacture of a hydrocyanation catalyst comprising, in particular, nickel values and a water-soluble phosphine.

Description of the Prior Art:

[0005] The hydrocyanation reaction, in particular of organic compounds comprising at least one site of ethylenic unsaturation, is an important industrial reaction permitting the preparation of numerous compounds. Thus, this reaction is employed in the synthesis of organic intermediates, such as 3-pentenitrile, which is converted into monomers such as aminocapronitrile or hexamethylenediamine.

[0006] This reaction is described, in particular, in French Patents No. 1,599,761 and No. 2,338,253 and in United States Patents Nos. 3,655,723, 3,850,973, 3,925,445 and 3,686,264.

[0007] This reaction is generally carried out in the presence of a catalyst comprising a transition metal. Such catalysts are also described in the above patents.

[0008] Thus, French Patent No. 2,338,253 describes a nickel-based catalyst which is formed by an aqueous solution of a water-soluble phosphine comprising nickel values.

[0009] This catalyst is obtained via addition, to an aqueous solution of phosphine, of a nickel compound which is soluble or insoluble in water. The amount of nickel in the aqueous phase then corresponds to that of nickel extracted or complexed by the water-soluble phosphine compound. However, in a preferred embodiment, it is advantageous to employ a nickel compound which is soluble in the phosphine/water mixture. Thus, French Patent No. 2,338,253 specifies that the nickel cyanide compound, which is insoluble in water but soluble in the aqueous solution of phosphine, is a preferred compound in the manufacture of such a catalyst. Other compounds, such as organic complexes or salts of nickel, can advantageously be employed to produce the catalyst.

[0010] These various methods for the preparation of a hydrocyanation catalyst exhibit the major disadvantage of requiring a nickel compound which may be either very difficult to manufacture with a sufficient degree of purity, or may

have a cost and an availability which adversely affect the economics of the industrial scale operation of the hydrocyanation reaction.

SUMMARY OF THE INVENTION

[0011] Accordingly, a major object of the present invention is the provision of an improved process for the manufacture of high purity hydrocyanation catalysts from readily available nickel compound starting materials, and which avoids or conspicuously ameliorates the above disadvantages and drawbacks to date characterizing the state of this art.

[0012] Briefly, the present invention features a process for the preparation of a catalyst for the hydrocyanation of organic compounds constituted by an aqueous solution of at least one water-soluble phosphine and of nickel, comprising contacting an aqueous solution of a water-soluble phosphine with nickel hydroxide, then adding hydrogen cyanide or a compound which generates hydrogen cyanide to the mixture, maintaining the mixture stirred until the nickel has dissolved and thence subjecting the mixture to a reduction in order to at least partially convert the dissolved nickel to the 0 oxidation state.

DETAILED DESCRIPTION OF BEST MODE AND SPECIFIC/PREFERRED EMBODIMENTS OF THE INVENTION

[0013] More particularly according to the present invention, in a preferred embodiment thereof, the reaction mixture, after addition of the hydrogen cyanide, is maintained under stirring at a temperature of less than 100°C, preferably ranging from 20°C and 80°C.

[0014] The amount of hydrogen cyanide added is at least equal to the stoichiometric amount for converting the nickel hydroxide into nickel cyanide.

[0015] The amount of hydrogen cyanide added will advantageously range from 30% to 200% greater than the stoichimetric amount.

[0016] After at least partial dissolution of the nickel hydroxide, the aqueous solution is subjected to a stage of reduction of the nickel with an oxidation state of greater than zero in order to obtain nickel in the zero oxidation state.

[0017] This reduction reaction is advantageously carried out after addition, to the mixture, of a small amount of nickel in the zero oxidation state. Such addition can be carried out by the addition of a small amount of catalyst comprising nickel in the zero oxidation state.

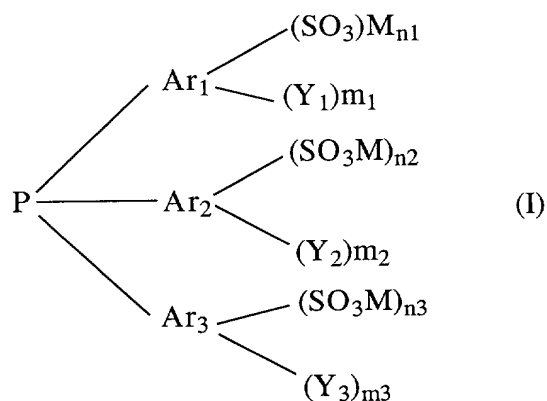
[0018] The stage of regeneration of the catalyst, or, stated differently, the reduction of the nickel to the 0 oxidation state, can be carried out by several processes, such as a reduction by gaseous hydrogen, an electrochemical reduction, or addition of an organic or inorganic reducing agent. The reduction processes are known and are described, in particular, in WO 97/24184, EP 0,715,890 and FR 1,599,761.

[0019] The amount of nickel compound utilized is advantageously selected such that there is, per liter of reaction solution, from 10^{-4} to 1, and preferably from 0.005 to 0.5, mol of nickel.

[0020] The amount of water-soluble phosphine used to prepare the reaction solution is advantageously selected such that the number of moles of this compound with respect to 1 mol of nickel ranges from 0.5 to 2,000 and preferably from 2 to 300.

[0021] Suitable water-soluble phosphine compounds include those compounds described in FR-2,338,253 or in WO 97/12857 and EP 0,650,959. These are exemplary only and not limiting.

[0022] Thus, suitable phosphines according to this invention have the following structural formula (I):



in which Ar_1 , Ar_2 and Ar_3 , which may be identical or different, are each an aryl radical; Y_1 , Y_2 and Y_3 , which may be identical or different, are each an alkyl radical having from 1 to 4 carbon atoms, an alkoxy radical having from 1 to 4 carbon atoms, a halogen atom, a CN group, an NO_2 group, an OH group, an NR_1R_2 radical, wherein R_1 and R_2 , which may be identical or different, are each an alkyl radical having from 1 to 4 carbon atoms; M is an inorganic or organic cationic residue selected, such that the compound of formula (I) is soluble in water, from the group consisting of H^+ , cations derived from alkali metals or alkaline earth metals, $\text{N}(\text{R}_3\text{R}_4\text{R}_5\text{R}_6)^+$, wherein R_3 , R_4 , R_5 and R_6 , which may be identical or different, are each an alkyl radical having from 1 to 4 carbon atoms or a hydrogen atom, and other metal cations, the benzenesulfonic acid salts of which are soluble in water; m_1 , m_2 and m_3 which may be identical or different, are each an integer ranging from 0 to 5; and n_1 , n_2 and n_3 , which may be identical or different, are each an integer ranging from 0 to 3, at least one of these being equal to or greater than 1.

[0023] Exemplary metals, the benzenesulfonic acid salts of which are soluble in water, include lead, zinc and tin.

[0024] By the expression "soluble in water" is generally intended a compound soluble to at least 0.01 g per liter of water.

[0025] Preferred phosphines of formula (I) are those in which:
 Ar_1 , Ar_2 and Ar_3 are phenyl radicals;

Y_1 , Y_2 and Y_3 are alkyl radicals having from 1 to 2 carbon atoms, or alkoxy radicals having from 1 to 2 carbon atoms;

M is a cation selected from the group consisting of H^+ , cations derived from Na, K, Ca and Ba, NH_4^+ , and tetramethylammonium, tetraethylammonium, tetrapropylammonium and tetrabutylammonium cations;

m_1 , m_2 and m_3 are integers ranging from 0 to 3; and

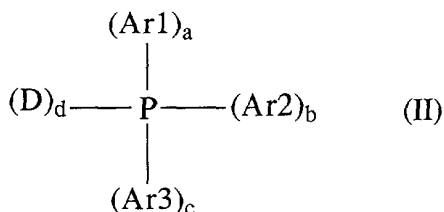
n_1 , n_2 and n_3 are integers ranging from 0 to 3, at least one also being greater than 1.

[0026] The more particularly preferred phosphines are the sodium, potassium, calcium, barium, ammonium, tetramethylammonium and tetraethylammonium salts of mono(sulfo-phenyl)diphenylphosphine, di(sulfo-phenyl)phenylphosphine and tri(sulfo-phenyl)phosphine, in which the SO_3 groups are preferably in the meta-position.

[0027] Exemplary phosphines of formula (I) according to the process of the invention are alkali metal or alkaline earth metal salts, ammonium salts, or quaternary ammonium salts of (3-sulfo-4-methylphenyl)di(4-methylphenyl)phosphine, (3-sulfo-4-methoxyphenyl)di(4-methoxyphenyl)phosphine, (3-sulfo-4-chlorophenyl)di(4-chlorophenyl)phosphine, di(3-sulfo-phenyl)phenylphosphine, di(4-sulfo-phenyl)phenylphosphine, di(3-sulfo-4-methylphenyl)(4-methylphenyl)phosphine, di(3-sulfo-4-methoxyphenyl)(4-methoxyphenyl)phosphine, di(3-sulfo-4-chlorophenyl)(4-chlorophenyl)phosphine, tri(3-sulfo-phenyl)phosphine, tri(4-sulfo-phenyl)phosphine, tri(3-sulfo-4-methylphenyl)phosphine, tri(3-sulfo-4-methoxyphenyl)phosphine, tri(3-sulfo-4-chlorophenyl)phosphine, (2-sulfo-4-methylphenyl)(3-sulfo-4-methylphenyl)(3,5-disulfo-4-methylphenyl)phosphine or (3-sulfo-phenyl)(3-sulfo-4-chlorophenyl)(3,5-disulfo-4-chlorophenyl)phosphine.

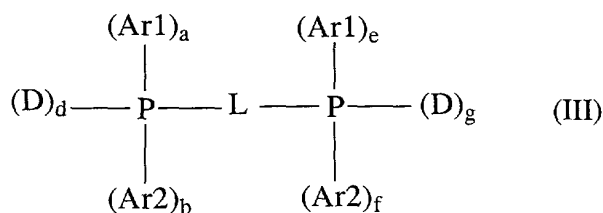
[0028] A mixture of these phosphines can of course be employed, in particular a mixture of mono-, di- and tri-meta-sulfonated phosphines.

[0029] Monodentate and bidentate phosphines having the following structural formulae (II) and (III) are also suitable according to the present invention:



in which Ar1 and Ar2, which may be identical or different, are each aryl radicals or substituted such aryl radicals bearing one or more substituents, such as alkyl or alkoxy radicals having from 1 to 4 carbon atoms, halogen atoms, hydrophilic groups, such as -COOM, -SO₃M or -PO₃M, wherein M is an inorganic or organic cationic residue selected from among hydrogen, cations derived from alkali metals or alkaline earth metals, ammonium cations -N(R)₄, wherein the radicals R, which may be identical or different, are each a hydrogen atom or an alkyl radical having from 1 to 4 carbon atoms, and other cations derived from metals, the arylcarboxylic acid, arylsulfonic acid or arylphosphonic acid salts of which are soluble in water, -N(R)₄, wherein the radicals R, which may be identical or different, are each a hydrogen atom or an alkyl radical having from 1 to 4 carbon atoms, or -OH; Ar₃ is a substituted aryl radical bearing one or more substituents, such as alkyl or alkoxy radicals having from 1 to 4 carbon atoms, halogen atoms, hydrophilic groups, such as -COOM or -PO₃M, wherein M is an inorganic or organic cationic residue selected from among hydrogen, cations derived from alkali metals or alkaline earth metals, ammonium cations -N(R)₄, wherein the radicals R, which may be identical or different, are each a hydrogen atom or an alkyl radical having from 1 to 4 carbon atoms, and other metal cations, the arylcarboxylic acid or arylphosphonic acid salts of which are soluble in water, N(R)₄, wherein the radicals R, which may be identical or different, are each a

hydrogen atom or an alkyl radical having from 1 to 4 carbon atoms, or -OH, with the proviso that at least one of the substituents of Ar₃ is a hydrophilic group as defined above; a is 0 or 1; b is 0 or 1; c is an integer ranging from 0 to 3; D is an alkyl radical, a cycloalkyl radical or an alkyl or cycloalkyl radical substituted by one or more substituents, such as an alkoxy radical having from 1 to 4 carbon atoms, a halogen atom, a hydrophilic group, such as -COOM, -SO₃M or -PO₃M, wherein M is an inorganic or organic cationic residue selected from among hydrogen, cations derived from alkali metals or alkaline earth metals, ammonium cations -N(R)₄, wherein the radicals R, which may be identical or different, are each a hydrogen atom or an alkyl radical having from 1 to 4 carbon atoms, and other metal cations, the arylcarboxylic acid, arylsulfonic acid or arylphosphonic acid salts of which are soluble in water, -N(R)₄, wherein the radicals R, which may be identical or different, are each a hydrogen atom or an alkyl radical having from 1 to 4 carbon atoms, or -OH; d is an integer ranging from 0 to 3; and the sum (a+b+c+d) is equal to 3; and



in which Ar1, Ar2 and D are as defined above for the formula (II); a, b, e, and f are each 0 or 1; d and g are each an integer ranging from 0 to 2; the sum (a+b+d) is equal to 2; the sum (e+f+g) is equal to 2; and L is a single valency bond or a divalent hydrocarbonaceous radical, such as an alkylene radical, a cycloalkylene radical, an arylene radical, or a radical deriving from a heterocycle comprising one or two oxygen, nitrogen or sulfur atoms in the ring, these various cyclic radicals being bonded directly to one of the phosphorus atoms or both

phosphorus atoms or being bonded to one of the phosphorus atoms or to both via a linear or branched alkylene radical having from 1 to 4 carbon atoms, with the proviso that the ring or rings which are optionally moieties of the divalent radical L may comprise one or more substituents, such as an alkyl radical having from 1 to 4 carbon atoms.

[0030] By the expression "soluble in water" is intended a compound soluble to at least 0.01 g per liter of water.

[0031] Exemplary phosphines of structural formula (II) include tris(hydroxymethyl)phosphine, tris(2-hydroxyethyl)phosphine, tris(3-hydroxypropyl)phosphine, tris(2-carboxymethyl)phosphine, the sodium salt of tris(3-carboxyphenyl)phosphine, tris(3-carboxyethyl)phosphine, tris(4-trimethylammonioethyl)phosphine iodide, the sodium salt of tris(2-phosphonoethyl)phosphine or bis(2-carboxyethyl)phenylphosphine.

[0032] And exemplary phosphines of structural formula (III) include the sodium salt of 2,2'-bis[di(sulfophenyl)phosphino]-1,1'-binaphthyl, the sodium salt of 1,2-bis[di(sulfophenyl)phosphinomethyl]cyclobutane (CBDTS), 1,2-bis(dihydroxymethylphosphino)ethane, 1,3-bis(dihydroxymethylphosphino)propane, or the sodium salt of 2,2'-bis[di(sulfophenyl)phosphinomethyl]-1,1'-binaphthyl.

[0033] Certain of the water-soluble phosphines of formulae (I) to (III) are commercially available.

[0034] For the preparation of the others, reference is made to the general or specific processes for the synthesis of phosphines described in the general literature, such as Houben-Weyl, Methoden der organischen Chemie, "organische Phosphor Verbindungen" [Methods of Organic Chemistry, "Organic Phosphorus Compounds"], Part 1 (1963).

[0035] Lastly, for the preparation of water-soluble derivatives which have not been described, starting from phosphines not comprising water-soluble substituents described above, one or more of these hydrophilic substituents are

[0036] The ethylenically unsaturated organic compounds which can be subjected to hydrocyanation in the presence of a catalyst prepared according to the process of the invention are typically diolefins, such as butadiene, isoprene, 1,5-hexadiene or 1,5-cyclooctadiene; ethylenically unsaturated aliphatic nitriles, particularly linear pentenenitriles, such as 3-pentenenitrile or 4-pentenenitrile; monoolefins, such as styrene, methylstyrene, vinylnaphthalene, cyclohexene or methylcyclohexene; and mixtures of several of these compounds.

[0038] Not insignificant amounts of 2-methyl-3-butenitrile and 2-methyl-2-butenitrile are formed, with the linear pentenenitriles, during the hydrocyanation of butadiene.

[0040] The hydrocyanation reaction is generally carried out at a temperature ranging from 10°C to 200°C and preferably from 30°C to 120°C.

[0042] The hydrogen cyanide employed can be prepared from metal cyanides, in particular sodium cyanide, or from cyanohydrins.

[0043] The hydrogen cyanide is introduced into the reactor in the gaseous state or in the liquid state. It can also be dissolved beforehand in an organic solvent.

[0044] As regards a batchwise process, it is possible to charge into a reactor which has been purged beforehand using an inert gas (such as nitrogen or argon) either an aqueous solution comprising all or a fraction of the various constituents, such as the water-soluble phosphine, the transition metal compound, the optional reducing agent and the optional solvent, or introducing said constituents separately. Generally, the reactor is then heated to the desired temperature and then the compound to be hydrocyanated is introduced. The hydrogen cyanide is then itself introduced, preferably continuously and uniformly.

[0045] When the reaction (the progress of which can be monitored by quantitative determination of samples withdrawn) has been completed, the reaction mixture is withdrawn after cooling and the reaction products are isolated by separation via settling, optionally followed by extraction of the aqueous layer with an appropriate solvent, such as, for example, the abovementioned water-immiscible solvents.

[0046] The aqueous catalytic solution can then be recycled to a fresh reaction for the hydrocyanation of organic compounds comprising at least one ethylenic double bond, after having been optionally treated by a regeneration process.

[0047] It is also possible to use the catalyst in combination with a Lewis acid.

[0048] The Lewis acid comprising the cocatalyst makes it possible in particular, in the case of the hydrocyanation of ethylenically unsaturated aliphatic nitrites, to improve the linearity of the dinitriles obtained, namely, the percentage of linear dinitrile with respect to all of the dinitriles formed, and/or to increase the lifetime of the catalyst.

[0055] Very particularly preferred Lewis acids include zinc chloride, zinc bromide, stannous chloride, stannous bromide, stannous chloride stabilized with

lithium chloride, stannous chloride stabilized with sodium chloride and zinc chloride/stannous chloride mixtures.

[0056] The Lewis acid cocatalyst employed generally constitutes from 0.01 to 50 mol per mole of nickel compound and preferably from 1 to 10 mol per mole.

[0057] As regards the implementation of the process of the invention, the catalytic solution employed for the hydrocyanation in the presence of Lewis acid can be prepared before it is introduced into the reaction region, for example by addition, to the aqueous solution of the water-soluble phosphine, of the appropriate amount of nickel hydroxide, of the Lewis acid and optionally of the reducing agent.

[0058] It is also possible, under the conditions of the hydrocyanation process of the present invention, and in particular by carrying out the reaction in the presence of the catalyst described above comprising at least one water-soluble phosphine and at least one nickel compound, to isomerize 2-methyl-3-butenitrile to pentenenitriles in the absence of hydrogen cyanide.

[0059] The 2-methyl-3-butenitrile subjected to the isomerization according to the invention can be employed alone or as a mixture with other compounds.

[0060] Thus, it is possible to employ 2-methyl-3-butenitrile as a mixture with 2-methyl-2-butenitrile, 4-pentenenitrile, 3-pentenenitrile, 2-pentenenitrile, butadiene, adiponitrile, 2-methylglutaronitrile, 2-ethylsuccinonitrile or valeronitrile.

[0061] Thus, it is particularly advantageous to treat the reaction mixture originating from the hydrocyanation of butadiene with HCN in the presence of an aqueous solution of at least one water-soluble phosphine and of at least one nickel compound, more preferably of a nickel compound in the 0 oxidation state, as described above.

[0062] In this preferred embodiment, as the catalytic system is already present for the hydrocyanation reaction of butadiene, it is sufficient to terminate

any introduction of hydrogen cyanide in order to allow the isomerization reaction to take place.

[0063] It is possible, if appropriate in this embodiment, to gently flush the reactor using an inert gas, such as nitrogen or argon, for example, in order to drive off the hydrocyanic acid which might still be present.

[0064] The isomerization reaction is generally carried out at a temperature of from 10°C to 200°C and preferably from 60°C to 120°C.

[0065] In the preferred embodiment of an isomerization immediately following the hydrocyanation reaction of butadiene, it will be advantageous to carry out the isomerization at the temperature at which the hydrocyanation has been carried out.

[0066] As regards the process for the hydrocyanation of ethylenically unsaturated compounds, the catalytic solution used for the isomerization can be prepared before it is introduced into the reaction zone, for example by addition, to the aqueous solution of a water-soluble phosphine, of the appropriate amount of nickel compound and optionally of the reducing agent. It is also possible to prepare the catalytic solution in situ by simple mixing of these various constituents. The amount of nickel compound and the amount of water-soluble phosphine are the same as for the hydrocyanation reaction. This catalyst can also be prepared by the process of the invention before it is introduced into the reaction zone.

[0067] Although the isomerization reaction is generally carried out without a third solvent, it can be advantageous to add an inert water-immiscible organic solvent which can be that of the subsequent extraction. This is, in particular, the case when such a solvent has been employed in the hydrocyanation reaction of butadiene which has been used to prepare the mixture subjected to the isomerization reaction. Such solvents are advantageously selected from among those which have been indicated above for the hydrocyanation.

[0068] At the end of the reaction, it is very easy to separate the catalyst from the isomerization reaction products, as has been indicated for the hydrocyanation, and to recycle it, if appropriate, in one of the hydrocyanation reactions described above or in a fresh isomerization reaction, after treatment of the aqueous phase and/or of the solid phase according to the process of the invention with hydrogen cyanide in order to dissolve said solid phase.

[0069] In order to further illustrate the present invention and the advantages thereof, the following specific examples are given, it being understood that same are intended only as illustrative and in nowise limitative.

EXAMPLE 1:

[0070] 150 cm³ of a 1 mol/liter aqueous nickel chloride solution were charged into a 1 liter Erlenmeyer flask equipped with a magnetic bar. 170 cm³ of a 2 mol/liter aqueous sodium hydroxide solution were introduced, with stirring at room temperature, over a period of 3 hours and then the mixture was maintained stirred for 1 hour. The system was subsequently maintained standing for the time necessary for the nickel hydroxide precipitated to settle out and for the supernatant aqueous solution to become clear. The nickel hydroxide precipitate was then washed. To accomplish this, as much as possible of the supernatant aqueous phase was siphoned off, 200 ml of distilled water were added, stirring of the system was resumed for 1 hour and then the system was again maintained standing for the time necessary for the separation by settling of the solid phase; this series of operations was repeated until a supernatant aqueous phase of neutral pH was obtained. The solid phase was then recovered by filtration through a sintered glass of porosity 4. Said filtration was carried out so as to obtain the nickel hydroxide in the form of a paste which will be subsequently described as freshly precipitated and wet nickel hydroxide. Quantitative determination of the Ni on 3

withdrawn samples of this wet paste stored in a closed container resulted in a mean assay by weight of 25.2 wgt % of Ni.

[0071] 57.5 g of a 30 wgt % solution of sodium salt of trisulfonated triphenylphosphine (TSTPP) in water were charged into a 150 cm³ glass reactor purged with argon and equipped with an auto-suction turbine. This solution was degassed. 1.445 g of freshly precipitated and wet nickel hydroxide obtained above were subsequently introduced. With stirring (1,200 revolutions/minute) and at room temperature, 0.640 ml of hydrocyanic acid was injected into the reactor head space, with a constant flow rate and over a duration of one hour, via a syringe thermostatically controlled at -10°C. During the injection of the HCN, the solution rapidly became orangey and then red. After injection, the mixture was maintained stirred for 3 hours at 80°C and then cooled to room temperature, where it was maintained stirred for 12 hours. After flushing the head space of the reactor with argon for approximately 1 hour, a homogeneous and clear solution with a dark red coloration was recovered. Quantitative determination of the Ni on a withdrawn sample filtered by means of a Millipore Millex-HV® filter (Hydrophilic PVDF, 0.45 µm) provided the following result: 106 mmol/kg.

[0072] The solution thus recovered could be used as catalytic solution after having been subjected to a stage of electrochemical reduction after addition of nickel in the (0) oxidation state.

EXAMPLE 2:

[0073] 57.8 g of a 30 wgt % solution of sodium salt of trisulfonated triphenylphosphine (TSTPP) in water were charged into a 150 cm³ glass reactor purged with argon and equipped with an auto-suction turbine. This solution was degassed. 606 mg of a commercial nickel hydroxide (Aldrich) comprising approximately 61 wgt % of Ni were subsequently introduced. With stirring (1,200 revolutions/minute) and at room temperature, 0.640 ml of hydrocyanic acid

was injected into the reactor head space, with a constant flow rate and over a duration of one hour, via a syringe thermostatically controlled at -10°C . During the injection of the HCN, the solution rapidly became orangey and then red. After injection, the mixture was maintained stirred for 3 hours at 80°C and then cooled to room temperature, where it was maintained stirred for 12 hours. After flushing the head space of the reactor with argon for approximately 1 hour, a homogeneous and clear solution with a dark red coloration was recovered. Quantitative determination of the Ni on a withdrawn sample filtered by means of a Millipore Millex-HV[®] filter (Hydrophilic PVDF, $0.45\ \mu\text{m}$) provided the following result: 103 mmol/kg.

[0074] The solution thus recovered could be used as catalytic solution after having been subjected to a stage of electrochemical reduction after addition of nickel in the (0) oxidation state.

[0075] While the invention has been described in terms of various specific and preferred embodiments, the skilled artisan will appreciate that various modifications, substitutions, omissions, and changes may be made without departing from the spirit thereof. Accordingly, it is intended that the scope of the present invention be limited solely by the scope of the following claims, including equivalents thereof.